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(54) Title: GLYCOL-FREE FROST RESISTANT COOLING LIQUIDS

(57) Abstract

The invention concerns a frost resistant and heat-transference liquid on potassium-acetate and potassium-formate basis, containing as erosion- and corrosion hindering components 4-6 mass% glycerine, 0.8-0.9 mass% alkali-benzoate, 0.08-0.12 mass% alkali-polymetaphosphates, 0.02-0.04 mass% borax. The concentration of the erosion- and corrosion hindering components is kept at the optimum level, regardless of the liquid's water content and in a given case 0.15-0.20 mass% benzo-or tolyl-triazole.

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Glycol-free frost resistant cooling liquids

Technical Field

The invention relates to glycol-free, frost resistant cooling and heat transference liquids on potassium-acetate - potassium formate basis, as improvement to the solution of Hungarian patent No. 203 776, having the same subject matter. Said patent gives detailed discussion and summary of the state of the prior art and indicates the task aiming at a more advantagous satisfaction of need compared to it. The goal to be achieved by the present patent application lies in an improvement by modificating of the liquid's composition ensuring an efficacious protection against corrosion even if having been mixed with usually applied cooling liquids on glycol basis and meeting the more exacting hygienic requirements in heat exchangers of water for consumption as well as in heating systems, such as in radiators. This way of operation occures in heat supplying systems where the continuous running in winter is not needed in or it is not economical (e.g. work-shops, storerooms, week-end houses, certain public-buildings). When running discontinuously in winter, the water, as heat transferring medium, cannot be taken into account because of the frost-hazard of the equipment and fittings. Hence, the elaboration of a liquid proper from technical and hygienic points of view alike is necessitated also by the reqirements of the energy economy.

Background Act

The specification of the Hungarian patent referred above underlines (see p. 3, column 2, lines 20 to 22) that working out of a new inhibitor composition has not been intended, since the generally known inhibitors ensured a satisfactory protection to the new liquid as well. The further experiences,

however, showed that mixing the new liquid compositions with traditional antifreezes prepared on glycol basis is unavoidable e.g. at after-fillings or at incomplete rinsing of the container when changing the liquid. Still, this leads to the increase in the mixture's corrosivity at such a degree in the course of time (owing the polymerization and acid decomposition of the glycol component) that cannot occur when using the liquid according to the invention independently. Although even the cited patent emphasizes that the blending of the liquid compositions according to the invention with an antifreeze prepared on glycol basis is not advantageous and not recommended because of the risk of the available ecologic. hygienic as well as heat-technologic and other technical advantages. The practice supported that the blending, as reality, must be taken into account which, however. makes to be necessary the elaboration of a proper, new inbibitor composition.

Disclosure of Invention

One of the basic emphasized goals to be achieved by the liquid compositions according to the present invention is the environment and health protection. According to the international qualification of the new liquid, it has been classified into the mildest, i.e. into the No. „4" poison-group and the necessary precautionary measures are to be taken in compliance with it. Since the heat tranference functions treated necessitate a still milder (i.e. „free") qualification on account of the heat tranference liquid occasional mixing with the water of consumption due to the incomplet staunchness, to break-down or metallic elements' demage, the elaboration of such a liquid variety proved necessary, that, in addition to the corrosion safety needed, lags behind even the poison category which can be tolerated in internal

combustion engines and, at the same time, can meet the heat-technologic requirements as well.

The achievement of the aim set recently could be based on the observation that, if a water-soluble lubricant, preferably glycerine is added to the heattransferene liquid in a ratio of about 4 to 6 mass%, this lubricant, besides protecting the mobile metallic surfaces against friction, can impede the formation of the local concentration cells and, in this way, so can the possibility of the pitting and crevice corrosion even at identic inhibitor composition by ensuring the uniform distribution of the inhibitors in the adhering liquid film. It has been found that less glycerine than given above is not satifactory to provide a significant improvement of the protecting effect, whilst a greater quantity thereof would not be reasonable. since (apart from the expenses) it would decrease in the heat-transference coefficient in the temperature range under the freezing point of the water.

Another important observation serving as basis to the invention has been the compatibility of the glycerine additive mentioned with the efficacious inhibitor components, e.g. the widely used combination of the sodium-polyphosphates and borax. Applying these components and keeping the sodium-benzoate and benzo-triazole (the latter may be replaced by tolyl-triazole if required), it could be attained. that the rate of the galvanic (in other words „contract") corrosion lags behind the limit determined in the international standards even if the liquid. mixed with glycol, has been working during several years and having covered even several hundred thousand kms. This ensures, as a matter of fact. that the cooling circuit can last out the lifetime of the vehicle without renewal.

This ensures, as a matter of fact, that the cooling circuit can last out the life-time of the vehicle without renewal.

As a further contribution for the solution to the additional task having been set has been the consideration that in the heat supplying systems the variety of the metallic species brought into contact with each other is smaller than in the vehicles and the drastic fluctuation of the temperature is less frequent and, consequently, so is the corrosion activating heat-shock. On the other hand, when applying of such destination, the mixing with glycol cannot occur, and also on this account, some inhibitor components can be omitted without running the risk of enhanced corrosion. These are first of all, as far as the health hazard is concerned, albeit not significant (because of their small concetration), but not completely negligible, the triazoles. Accordingly, two types of inhibitor compositions proved suitable depending on whether the liquid will be used as

- antifreeze for vehicles, or
- heat-transference liquid in household or industrial equipment.

Depending on the said conditions, the liquid may contain in a given case besides the glycerine and the usual quantity of the other inhibitors listed, benzo-and tolyl-triazole respectively.

Best Mode for Carrying Out the Invention

Also the present invention is characterized in that the frost resistant cooling and heat-transference liquids contain as erosion-and corrosion hindering components 4-6 mass% glycerine, 0,8-0,9 mass% alkali-benzoate, 0,08-0,12 mass% alkali-polymetaphosphate and 0,02-0,04 mass% borax, and in a given case 0,15-0,20 mass% benzo-or tolyl-triazole.

Industrial Applicability

Although the data treated - with full knowledge of the given requirements and of the cited Hungarian patent - give due instructions to produce the liquid compositions, the following examples can serve for a closer elucidation of the improved invention.

Example 1

Moderately frost resistant cooling liquid variety

One ton liquid is produced by blending of 649,3 kg water, 189,4 kg caustic potash solution of 50 w%, 84 kg acetic acid solution of 96 w%, 16 kg formic acid solution of 99 w%, 50 kg glycerine of technical quality, 8,3 kg sodium-benzoate, 1,7 kg tolyl-triazole, 0,5 kg sodium-trimeta-phosphate, 0,5 kg sodium-hexametaphosphate and 0.3 kg borax (dissolving under stirring and cooling). The concentration of the acids and that of the alkali may obvisously be different from that as it is given above. If so, the proportions are to be varied according to the sense. The crystal point of the liquid produced in this way (in other words: its theoretic, i.e. thermodynamic freezing point) is -10°C but the separated, loose crystals containing liquid can be used even at -16°C (lower temperature limit).

Example 2

Middling frost resistant cooling liquid variety

To produce one ton liquid, 522,1 kg water, 272,6 kg caustic potash of 50 w%, 121 kg acetic acid of 96%, 23 kg formic acid of 99 w% is blended in the same way as described in Example 1. The quantity of the further components is identic. The crystal point of the liquid produced in this way is -23°C, its lower temperature limit, however, is -36°C.

Example 3

Cooling liquid variety frost resistant in an increased degree

To one ton of the make 216.1 kg water is blended with 472,6 kg caustic potash of 50 w%, 210 kg acetic acid of 96% and 40 kg formic acid of 99 w%, the further components are unchanged. The crystal point of the liquid produced in this way is -45°C, its lower temperature limit, however, is -70°C.

In knowledge of the above examples optional other varieties can also be manufactured by interpolation, according to the prescribed frost resistance. The given freezing points do not practically change if the liquids are blended with ones on glycol basis of identic freezing point. The mixing of liquids of different freezing point results in freezing point that can be estimated by proportionate interpolation. Another important advantage of the inhibotor composition elaborated is inherent in its compatibility with the inhibitors generally used in antifreeze makes on glycol basis. All these enables to keep the inhibitors' concentration constant, independently of that of the freezing point depressants, as shown in the examples. In this way it can be attained, that the liquid is not diluted with respect to the inhibitors but will contain their optimum concentration. regardless of whatever dilution needed corresponding to the lesser frost resistance requirement.

Example 4

Middling frost resistant liquid of health safety in an increased degree

To one ton of the product 523,8 kg water, 272,6 kg caustic potash of 50 w%, 121 kg acetic acid of 96 w%. 23 kg formic acid of 99 w%, 50 kg glycerine, 8,3 kg sodium-benzoate. 0.5 kg sodium-trimetaphosphate, 0,5 kg

sodium-hexametaphosphate and 0,3 kg borax are to be blended. The crystal point of the liquid is -23°C, whilst its lower temperature limit is -36°C.

The pH of the liquids manufactured in the treated way is in any case in the range of 8,7 ± 0,1. If there is a departure therefrom due to the fluctuation of the components' water content, a small quantity of acid or alkali is to be added to set the pH prescribed.

With the liquid improved according to the invention, hot and cold immersion glassware and highway corrosion tests have been carried out by Applicants and by other persons skilled in the art, including international acredited institutes. It has been pointed out that the limit values prescribed in the international standards (e.g. ASTM, BS) are met with high security and long-lasting. Besides, the corrosion occurring in a degree not attaining the limit values, is uniform, i.e. does not lead to perforation and neither to pittings or crevice.

What we claim is:

1. Frost resistant cooling and heat-transference liquid on potassium-acetate - potassium-formate basis, *characterized in that* the liquid contains as erosion-and corrosion hindering components 4-6 mass% glycerine, 0,8-0,9 mass% alkali-benzoate, 0,08-0,12 mass% alkali-polymetaphosphate, 0,02-0,04 mass% borax and in a given case 0,15-0.20 mass% benzo-or tolyl-triazole.

2. Frost resistant and heat-transference liquid according to claim 1, *characterized in that* the concentration of the erosion-and corrosion hindering components, independently of that of the acetate-and formate salts, is kept constant, even if the water content of the liquid is changed.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C09K 5/00
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

STN, REGISTRY, CA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 5079036 (ROE ET AL), 7 January 1992 (07.01.92), claims 1,8 --	1-2
A	EP, A1, 0345613 (HOECHST AKTIENGESELLSCHAFT), 13 December 1989 (13.12.89), claim 3 --	1-2
A	EP, A1, 0573287 (TEXACO CHEMICAL COMPANY), 8 December 1993 (08.12.93), page 3, line 38 - line 45 --	1-2

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A1, 0306972 (ESZAKMAGYARORSZAGI VEGYIMÜVEK), 15 March 1989 (15.03.89), claim 1	1-2

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INTERNATIONAL SEARCH REPORT

Information on patent family members

01/04/96

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 5079036	07/01/92	CA-A- 2045377	28/01/92
EP-A1- 0345613	13/12/89	DE-A,A- 3819353	14/12/89
EP-A1- 0573287	08/12/93	NONE	
EP-A1- 0306972	15/03/89	DE-A- 3871668 JP-A- 1103684	09/07/92 20/04/89